



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C04B 18/08	A1	(11) International Publication Number: WO 90/11977 (43) International Publication Date: 18 October 1990 (18.10.90)
(21) International Application Number: PCT/NO90/00063 (22) International Filing Date: 9 April 1990 (09.04.90) (30) Priority data: 891463 10 April 1989 (10.04.89) NO (71) Applicant (for all designated States except US): DEN NORSKE STATS OLJESELSKAP A.S [NO/NO]; Forus, Postboks 300, N-4001 Stavanger (NO). (72) Inventor; and (75) Inventor/Applicant (for US only) : VASSØY, Bjørn [NO/NO]; Fagerstølveien 8, N-4027 Stavanger (NO). (74) Agent: LÆRUM, Martin; Den Norske Stats Oljeselskap a.s, Forus, Postboks 300, N-4001 Stavanger (NO).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), SU, US. Published <i>With international search report.</i> <i>In English translation (filed in Norwegian).</i>
(54) Title: PROCEDURE FOR THE ADMIXTURE OF SILICON OXIDE TO A HYDRAULIC CEMENT SLURRY (57) Abstract <p>The invention relates to a procedure for the admixture of silicon oxide to a hydraulic cement slurry, particularly for well cementing, and is characterized by amorphous silica with particles smaller than 1 micro-metre being mixed with water to a liquid micro-silica, silica flour with particles from 2 to 200 micro-metres being mixed in said liquid micro-silica and the thereby obtained silica mixture being added to cement slurry directly in a mixing tank. In addition the invention relates to a hydraulic cement slurry produced according to the procedure.</p>		

PROCEDURE FOR THE ADMIXTURE OF SILICON OXIDE TO A HYDRAULIC CEMENT SLURRY.

The present invention relates to a procedure for the admixture of silicon oxide to a hydraulic cement slurry.

5

In addition, a hydraulic cement slurry produced according to said procedure.

This type of hydraulic cement slurry is primarily used in
10 hydrocarbon wells and in geo-thermal wells.

Cement slurries with silicon oxide admixture are typically used in oil well cement where their primary purpose is to prevent reduction of cement slurry strength over time,
15 particularly at high pressure and temperatures exceeding 100°C.

In connection with primary cementing of hydrocarbon wells, cement slurries are pumped down through casings in the well,
20 and up on the outside, filling the annulus between the casing and borehole wall. The major purposes of the cementing are:

- 1) Support and protect the casing.
- 25 2) Isolate weak structures or high-pressure zones.
- 3) Prevent water, oil or gas from moving between structures or up to the surface.

BACKGROUND ART

30

When exposed to temperatures above 100°C over an extended period, an ordinary cement slurry used in hydrocarbon wells will gradually lose its pressure strength at the same time as its permeability increases. These properties increase
35 with increasing temperature.

At temperatures above 130°C, this may occur after just 24 hours. This may develop to a stage where the cement crumbles and thus loses its function.

At temperatures above 100°C, the ordinary C-S-H (calcium-silicate-hydrate) binding turns to alpha-calcium-silicate-hydrate. Thus, the strength is reduced, and the permeability increases.

5

In order to prevent this reaction, it is normal to add SiO₂, silicon oxide, in the cement slurry. SiO₂ prevents the formation of alpha-calcium-silicate-hydrate. Instead, mono-calcium-silicate-hydrate is formed, which is a more
10 stable binding. Thus, the strength is maintained. The most common way of adding the cement slurry SiO₂ is to add silica flour and silica sand. Both substances mainly consist of SiO₂.

15 Silica flour is a light grey/white powder produced from quarts. It is produced both in Europe and the U.S., and has a number of product names such as "SSA-1" from Halliburton Services, "D-66" from Dowell Schlumberger or "D-8" from B.J. Hughes. The specific weight is approx. 2.63 gcm⁻³. The
20 grain size is between 2 and 200 micro-metres, approx. 50 weight% being less than 50 micro-metres. This is more or less the same grain size as oil well cement.

The silica sand is much more coarse-grained than silica
25 flour. The size of the grains is usually from 1 to 2 mm. Also silica sand is produced from quarts and has a specific weight of approx. 2.63 gcm⁻³.

Silica flour is definitely the most common of these. In
30 order to prevent strength reduction in the cement slurry, minimum 35 % silica flour must be used based on the weight of cement.

This silica flour is today mixed dry with the dry cement in
35 silos onshore. This is done by blowing each dry substance with pressurized air from its respective silo into a third silo. Subsequently, the mixture is blown back and forth between two silos. This results in a somewhat homogeneous

mixture. This blowing, however, deteriorates the properties of the finished cement slurry since the pressurized air contains small amounts of water. The properties that are deteriorated are: free water is increased, the filter loss increases and the setting time increases. These properties are all critical to a cement slurry.

With this mixing method, it is very difficult to get an accurate dosaging of the various components. This is due to the fact that measuring accurate amounts of dry substances represents a measurement-technical problem. In addition, there are problems obtaining a homogeneous and stable mixture.

The prior art also requires separate storage silos on the rigs for the storage of the dry mixture. This may in many cases involve problems due to poor silo capacity. In addition, so much dry mixture is mixed that there is enough for two jobs (100 % backup). What remains after the cementing job is done, is usually used in cement slurries that do not require such silica flour. The objective of this is to rid of the mixture, thus making the storage silo available for ordinary cement. This is rather unfavourable from an economic point of view.

Recently, it has been realized that the admixture of micro-silica also prevents reduction of strength at high temperatures. Micro-silica reacts the same way as silica flour in a cement slurry exposed to high temperatures. Also here, mono-calcium-silicate-hydrate is formed.

Silica dust collected from electro-thermal melting furnaces that produce at least 75 % ferrosilicon (Si contains at least 76 %) is preferably used as micro-silica, but dust from furnaces that produce 50 % ferrosilicon may also be used as a basis material for the present invention.

It is also possible to obtain silicon dust as a main product from the said melting furnaces by adjusting the reduction conditions. This type of amorphous silica can also be synthetically produced without reduction and re-oxidation. 5 Alternatively, a silica dust generator can be used for the production of silica fines, or silica may be produced by precipitation.

In order for micro-silica to be easily transportable, the 10 producer mixes it with approx. 50 weight% of fresh water. A liquid micro-silica with a specific weight of approx. 1.40 gcm⁻³ is then obtained. Elkem has e.g. given this mixture the product name "EMSAC 460S".

15 According to a known method, the cement slurry density must be reduced from approx. 1.90 gcc to approx. 1.70 gcc in order to add a sufficient amount of liquid micro-silica.

Subsequently, the mixture must be weighed up again to the 20 desired density by means of weight materials. This is an inconvenient solution, even more serious, however, is the fact that this method gives a too viscous and thixotropic cement slurry.

25 The ph of the mixture is increased by another known method prior to adding all of the cement, thus allowing 35 % micro-silica to be added. Consequently, the tiny micro-silica particles flocculate, and this gives a non-gas-tight cement slurry. In addition, also this method 30 gives a too viscous and thixotropic cement slurry.

Object of the invention

The purpose of the present invention is to provide an 35 improved procedure for the admixture of silicon oxide where the above-mentioned problems are overcome.

THE PRESENT INVENTION

This, according to the present invention, is obtained by a procedure characterized by:

- 5
- amorphous silica with particles of less than 1 micro-metre being mixed with water to liquid micro-silica,
 - silica flour with particles from 2 to 200 micro-metres
10 being mixed in the liquid micro-silica and the thereby obtained silica mixture being added to a cement slurry directly in a mixing tank.

The invention also includes a hydraulic cement slurry which
15 contains 5 - 100 % silicon oxide additive containing liquid amorphous silica with particles of less than 1 micro-metre with a silica flour admixture, based on the weight of cement, 2 - 200 % light weight aggregate with a particle density of between 0.1 and 1.5 g/cm³, based on the weight of
20 cement, 0 - 5 % thinner (dry weight) based on the weight of cement, 1 - 10 % filter loss reducing agent (dry weight) based on the weight of cement, and water of such an amount that the cement slurry gets a density of between 0.8 and 2.0 g/cm³.

25

The amorphous silica dust used in the present invention mainly consists of submicron globular particles.

The silica dust particles may e.g. contain 60 - 100 weight%
30 of SiO₂ and have a density of 2.0 - 2.40 g/cm³ and a specific surface area of 15 - 30 m²/g. The particles are mainly globular and are less than 1 micro-metre in size. These values may of course vary. For example, the silica dust may have a lower SiO₂ content and the particle size
35 distribution may be adjusted, e.g. by coarse particles being removed.

Silica flour and liquid micro-silica are mixed so that the total of the two substances represents minimum 35 weight% of dry substance of the dry cement weight in a cement slurry. Thus, a reduction of strength at high temperature is prevented. The mixture of the 2 substances also gives good cement slurry properties, such as very low viscosity, minimal thixotropic properties, stable slurry, low filter loss and zero free water. In addition, slurries which contain more than a given amount of micro-silica have gas-tight properties.

The mixture of the two substances may be done onshore in a mixing plant. Since liquid micro-silica is one of the components, it can be measured with great accuracy. The silica flour is added in the liquid micro-silica until the desired density of the finished mixture is obtained. This gives an accurately composed mixture.

Other advantages of the invention:

- The mixture is entirely stable, even after several months' storage.
- The mixture pumpability is good and it may be added directly in a pre-mixing tank on rigs or directly in the mixing tanks on cement mixing units.
- Extra blowing of dry cement and silica flour from one silo to another is avoided.
- The mixture does not require a special storage tank on the rigs.
- Excessive amounts of the mixture can be returned onshore and stored for later use.

MODES FOR CARRYING OUT THE INVENTION

The invention will now be further described by means of the following examples.

Example 1

A silica mixture with the following composition was produced according to the present invention:

5

Silica flour, "SSA-1"	55.6 weight%
Micro-silica (50% dry substance)	44.4 weight%

The silica flour is "SSA-1" delivered by Halliburton
10 Services, Tananger. Micro-silica is "EMSAC 460S" from
Elkem, Bremanger Smelteverk (50 weight% of dry substance in
water).

The rheologic properties at 20°C were:

15 600rpm = 210cp, 300rpm = 126cp, 200rpm = 94cp, 100rpm =
53cp.

The mixture of silica flour and liquid micro-silica may
contain 5-80 weight% of silica flour, preferably 40-60
20 weight%, and 20-95 weight% of liquid micro-silica,
preferably 40-60 weight%.

In addition, all types of weight materials, dispersants,
retarders, accelerators, filter loss reducing substances,
25 weight-reducing substances and anti-foam agents may be added
to mixtures of silica flour in liquid micro-silica.

All types of materials used in oil well cement may be used
as weight materials, preferably hematite, ilmenite or
30 barite. The mixture may possibly contain 0-50 weight% of
weight material, chiefly 0-20 weight%.

All such agents known to be used as plasticizing, or super-
plasticizing, agents in cement-based systems may be used as
35 dispersants. For example agents based on lignosulfonates,
partly de-sulfonated lignosulfonates, polyhydroxyl-carboxyl
acids, sulfonated naphthalene-formaldehyde - or sulfonated
melamine-formaldehyde products.

The mixture may possibly contain 0-10 weight% of dispersant (based on dry substance), chiefly 0-2 weight%.

The mixture according to the present invention may contain 5 retarders such as cellulose derivates, sugar derivates, ligno-sulfonates and lignins.

The mixture may possibly contain 0-10 weight% of retarder based on dry substance, preferably 0-2 weight%.

10

Sodium chloride (NaCl) and calcium chloride (CaCl_2) may be used as accelerator.

The mixture may possibly also contain 0-10 weight 15 accelerator, preferably 0-2 weight%.

The mixture according to the present invention may contain filter loss reducing agents, e.g. agents based on amyl or amyl derivates, cellulose derivates such as carboxyl-ethyl- 20 cellulose, methyl-cellulose or ethyl-cellulose, or synthetic polymers such as polyacrylonitrile or polyacrylamide.

The mixture may possibly contain 0-10 weight% of filter loss reducing agent (based on dry weight), preferably 0-2 25 weight%.

Hollow glass balls are particularly preferred as weight-reducing agents. This type of light weight aggregate is available under a number of product names, e.g. hollow glass 30 balls produced by 3M Company, the U.S.

Also whole balls produced from shifting ashes may be used, e.g. the product "Fillite" produced by Fillite Ltd., England.

35

The mixture may possibly contain 0-50 weight% of weight reducing substances, preferably 0-30 weight%.

According to the present invention, fresh water or sea-water may be used as water. The mixture may possibly contain 0-50 weight% of water, preferably 0-20 weight%.

- 5 The mixture may be used in cement slurries based on all types of oil well cement described in API SPEC 10.

Example 2

- 10 A typical cement slurry where the silicon oxide mixture described above in this example is included:

Norcem G-cement	100 kg
Silica flour	25 kg
15 Micro-silica, 50% dry substance	20 kg
Filter loss reducing agent	7 l
Dispersant	0.5 kg
Retarder	0.97 kg
Fresh water	36.59 l

20

This cement slurry had the following characteristics:

Density:	1.90 g/cm ³
25 Silica flour, "SSA-1"	55.6 weight%
Micro-silica (50% dry substance)	44.4 weight%

The plastic viscosity was 84 cp, and the yield strength was 20.16 Pa.

30

The rheologic properties at 90°C:

300 rpm: 23 cp, 200 rpm: 17 cp, 100 rpm: 10 cp, 6 rpm: 1 cp.

35 API SPEC 10 filter loss: 34 cm³/30 min.

Pressure strength after 24 hours at 124°C: 216 bars.

Example 3

In order to compare the pressure strength of a cement slurry containing the silicon oxide mixture according to the present invention with a slurry according to known technology, two cement slurries, 1 and 2, with the following composition may be referred to:

Slurry 1: (According to known technology).

10

G-cement	100.0 kg
Liquid micro-silica	11.0 kg
Filter loss reducing substance	0.5 kg
Dispersant	3.0 l
15 Retarder	0.27 l
Anti-foam agent	0.20 l
Fresh water	36.40 l

The density of the slurry: 1.90 g/cm^3 .

20

Slurry 2: (according to the invention).

G-cement	100.0 kg
Silica flour	25.0 kg
25 Liquid micro-silica (50% dry substance)	41.7 kg
Filter loss reducing substance	10 l
Dispersant	0.5 kg
Retarder	0.4 kg
Anti-foam agent	0.2 l
30 Fresh water	78.86 l

The density of the slurry: 1.60 g/cm^3 .

The development of the pressure strength over time at 134°C was measured with an "Ultrasonic Cement Analyzer" (UCA), and the results are given in the table below:

11

Slurry UCA pressure strength at 134°C (bar)

no.	0.5 dg	1 dg	2 dg	3 dg	5 dg	7 dg	14 dg	28 dg
1	145	155	152	138	117	103	56	-
5 2	55	93	103	105	107	110	110	110

Slurry no. 2 gets lower pressure strength than no. 1 at the beginning due to lower specific weight of the slurry.

CLAIMS

1. Procedure for the admixture of silicon oxide to a hydraulic cement slurry, particularly for well cementing, characterized by
 - amorphous silica with particles smaller than 1 micro-metre being mixed with water to a liquid micro-silica,
 - silica flour with particles from 2 to 200 micro-metres being mixed in said liquid micro-silica,
 - the thereby obtained silica mixture being added to cement slurry directly in a mixing tank.
2. Procedure according to claim 1, characterized by 5 to 80 weight% of silica flour being added, preferably from 40 to 60 weight%, from 95 to 20 weight% of liquid micro-silica, preferably from 60 to 40 weight% based on the weight of dry substances, and from 0 to 50 weight% of water, preferably below 20 weight% based on the weight of dry substances, where the water may be fresh water or seawater.
3. Procedure according to claims 1 and 2 characterized by said silica flour and micro-silica together representing 35 weight% of the cement on the basis of dry substances in a cement slurry.
4. Hydraulic cement slurry for oil well cementing characterized by that it contains hydraulic cement, 5 - 100 % silicon oxide containing liquid amorphous silica with particles smaller than 1 micro-metre and with a silica flour admixture based on the weight of cement, 2 - 200 % light weight aggregate with a true particle density of between 0.1 and 1.5 g/cm³, based on the weight of cement, 0 - 5 %

13

thinner (dry weight) based on the weight of cement, 1 -
10 % filter loss reducing agent (dry weight) based on
the weight of cement, and water of such an amount that
the cement slurry gets a density of between 0.8 and 2.0
g/cm³.

5

5. Hydraulic cement slurry according to claim 4,
c h a r a c t e r i z e d b y this being produced
according to the procedure stated in claims 1-3.

10

INTERNATIONAL SEARCH REPORT

International Application No PCT/NO 90/00063

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 04 B 18/08														
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 04 B</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div> <p>SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	C 04 B								
Classification System	Classification Symbols													
IPC5	C 04 B													
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 10%; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="vertical-align: top;">A</td> <td>EP, A2, 0146912 (BIURO STUDIOW I PROJEKTOW ENERGETYCZNYCH "ENERGOPROJEKT") 3 July 1985, see the whole document --</td> <td style="vertical-align: top;">1-5</td> </tr> <tr> <td style="vertical-align: top;">A</td> <td>NO, B, 148995 (ELKEM A/S) 17 October 1983, see the whole document --</td> <td style="vertical-align: top;">1-5</td> </tr> <tr> <td style="vertical-align: top;">A</td> <td>DE, A1, 3522677 (HEINRICH ELSKES KG) 8 January 1987, see the whole document -- -----</td> <td style="vertical-align: top;">1-5</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	EP, A2, 0146912 (BIURO STUDIOW I PROJEKTOW ENERGETYCZNYCH "ENERGOPROJEKT") 3 July 1985, see the whole document --	1-5	A	NO, B, 148995 (ELKEM A/S) 17 October 1983, see the whole document --	1-5	A	DE, A1, 3522677 (HEINRICH ELSKES KG) 8 January 1987, see the whole document -- -----	1-5
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³												
A	EP, A2, 0146912 (BIURO STUDIOW I PROJEKTOW ENERGETYCZNYCH "ENERGOPROJEKT") 3 July 1985, see the whole document --	1-5												
A	NO, B, 148995 (ELKEM A/S) 17 October 1983, see the whole document --	1-5												
A	DE, A1, 3522677 (HEINRICH ELSKES KG) 8 January 1987, see the whole document -- -----	1-5												
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center;">9th July 1990</td> <td style="text-align: center;">1990 -07- 10</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center;">SWEDISH PATENT OFFICE</td> <td style="text-align: center;">May Hallne <i>May Hallne</i></td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	9th July 1990	1990 -07- 10	International Searching Authority	Signature of Authorized Officer	SWEDISH PATENT OFFICE	May Hallne <i>May Hallne</i>				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report													
9th July 1990	1990 -07- 10													
International Searching Authority	Signature of Authorized Officer													
SWEDISH PATENT OFFICE	May Hallne <i>May Hallne</i>													

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/NO 90/00063**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on **90-05-24**.
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0146912	85-07-03	JP-A- 60227818 US-A- 4618376	85-11-13 86-10-21
NO-B- 148995	83-10-17	NONE	
DE-A1- 3522677	87-01-08	NONE	